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THE IONIZATION PRODUCED BY HEATED SALTS.

L. C.

THESIS

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BY

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The Ionization produced by Heated Salts.

By CHARLES SHEARD, *M.A., Assistant Professor of Physics, Ohio State University, and Fellow in Physics, Princeton University*.*

INVESTIGATIONS have been made in recent years upon the existence of positive and negative emissions from heated salts and upon the values of e/m of the emitted ions. Many substances have been examined as to their ionizing

* Communicated by Professor O. W. Richardson. Read before the American Physical Society, New York Meeting, March 2nd, 1912. See Abstract, Phys. Rev. xxxv. pp. 234–236, 1912.

powers * and certain conclusions drawn which are indicated below. The relation † between the values of the currents and the temperature is generally that given by Richardson's ‡ formula

$$i = A\theta^{\frac{1}{2}}e^{-\frac{b}{\theta}}.$$

It seems likely that this formula always holds good, provided the chemical nature of the source of the ionization is unaffected by the temperature changes. The positive current-time relations show a rise to a maximum value of the current followed by decay with time, and are satisfactorily represented by a formula § of the type

$$i = A(e^{-\lambda_2 t} - e^{-\lambda_1 t}).$$

The only exceptions to this statement of which the writer is aware are the results of Schmidt's ‖ experiments with haloids of cadmium. Some substances apparently give copious positive and others abnormally large negative ionizations¶. Most of these experiments have been made with salts in contact with metallic plates, usually platinum. Garrett and Willows **, in repeating the work of Beattie †† upon the conductivity produced by heating common salt and iodine on an insulated zinc plate, concluded "that the metal is a necessary part to the changes causing the conduction." This is likewise the view held by W. Wilson ‡‡ in some recent investigations with aluminium phosphate. Furthermore, Horton §§ has advanced the view that molecules of CO gas, liberated from the glass walls of the containing vessel and diffusing into the surface of the metal, finally emerge in an ionized condition. It is important, then, that the ionization

* Some of the substances which have been found to produce ionization at temperatures of about 400° C. are listed in papers by Garrett (Phil. Mag. [6] xiii. p. 729, 1907) and Schmidt (*Ann. der Phys.* [4] xxxv. p. 404, 1911).

† Garrett & Willows (Phil. Mag. [6] viii. p. 437, 1904). A. E. Garrett (Phil. Mag. [6] xiii. p. 728, 1907).

‡ Proc. Camb. Phil. Soc. xi. p. 286, 1902, and Phil. Trans. 201, p. 516, 1903.

§ *Loc. cit.* under † and also A. E. Garrett (Phil. Mag. [6] xx. pp. 573–591, 1910).

‖ *Ann. der Phys.* [4] xxxv. p. 401 (1911).

¶ A. Wehnelt (Phil. Mag. [6] x. p. 80, 1905). J. J. Thomson (Camb. Phil. Soc. Proc. xiv. p. 105, 1907).

** *Loc. cit.*

†† Phil. Mag. [5] xlviii. p. 97 (1899) and [6] i. p. 442 (1901).

‡‡ Phil. Mag. [6] xxi. p. 634 (1911).

§§ Proc. Roy. Soc. ser. A. vol. lxxxiv. p. 433 (1910); Camb. Phil. Soc. Proc. xvi. p. 89 (1911).

effects from heated salts be examined, using apparatus which does not involve the heating of the salt in contact with metal.

The nature of the ionization process or processes has not been adequately investigated. Richardson * examined the positive ionization from several sulphates and phosphates by the "strip" and "tube" methods. The tube method gave no such diminution in the ionization at low pressures as was observed when the salts were heated on the platinum strip. These results are explicable if the ionization arises in part or in whole from the decomposition, not of the salt itself, but of an intermediate product. The results presented in this article will show that there is both an ionization of the salt vapour and an emission of ions from the salt.

Determinations of the specific charge† of the emissions from heated salts have shown positive ions characteristic of the base of the salts and electrons only. In this paper it will be shown that with fresh samples of cadmium iodide there is a large emission of negative ions when it is first heated. In general, the current-E.M.F. curves for the negative ionization are very similar to those for the positive. This indicates that the negative ions are comparable in mass with the positive ions. This point of view is confirmed by measurements, carried out about the same time by Professor Richardson ‡, of the value of e/m for the negative ions given out by the iodides of the alkaline earth-metals. The values found agreed with the view that the ions were atoms of iodine carrying a single electronic charge. I have not yet had an opportunity to investigate the effect of a magnetic field on the initial negative emission from cadmium iodide.

Apparatus and Methods of Experimentation.

Fig. 1 represents a form of apparatus used in the earlier experiments. It consisted of hard glass tubes, each 30 cm. long and 2·5 cm. internal diameter, joined by a cross-connexion of glass 2 cm. long and 1·5 cm. diameter. Each tube was closed with a ground-glass stopper, into which were sealed the electrodes. The outer electrodes were cylinders of platinum gauze each 6 cm. in length. When in place they fitted closely against the surfaces of the containing tubes. This ensured the heated tube and salt being at the potential of the gauze, and also prevented the passage

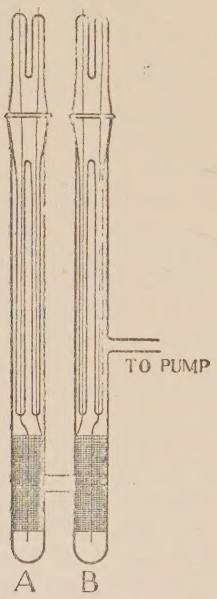
* Phil. Mag. [6] xxii. p. 669 (1911).

† Richardson (Phil. Mag. xx. p. 981, 1910). Davisson (Phil. Mag. xxiii. p. 121, 1912).

‡ Phys. Rev. xxxiv. p. 386 (1912).

of salt vapour between the outer glass walls and the gauze. The inner electrodes, centralized with respect to the outer ones, were of platinum wire 0·2 mm. in diameter. Each wire was sealed in glass; the lower 6 cm. only were left exposed.

Fig. 1.



The double-tube apparatus was heated in an electric oven, and was inserted into it some 10 centimetres above the electrodes. The furnace was first heated some 50° C. higher than the temperature desired, the tube was then introduced and the required temperature obtained in 3–5 minutes. This is important, particularly in determining the initial stages of the rise or decay of the ionization with time. By means of control resistances it was possible to keep the temperature constant within 5 degrees over several hours of experimentation.

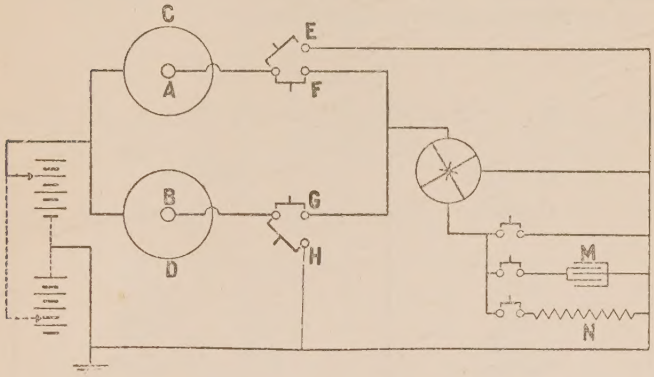
Before each test the main tubes and the electrodes were thoroughly cleansed with nitric acid, sulphuric acid, alcohol and ether mixture and distilled water, and then slowly dried. At temperatures between 350° C. and 500° C. and with potential of ± 200 volts applied at the outer electrodes, leakage currents were obtained which ranged in value from 1×10^{-13} to 1×10^{-11} ampere. These currents

were in general negligible in comparison with those obtained after the introduction of the salts.

The samples of salt investigated were inserted in the same half of the double-tube arrangement. In the presentation of results, the tube carrying the salt will be referred to as A and the "unsalted" one as B.

The connexions and method of operation are outlined in fig. 2. The outer electrodes, C and D, were connected to

Fig 2.



a source of high potential. The inner electrodes, A and B, were connected in turn to one pair of quadrants of the electrometer, or earthed, by means of suitable keys represented as E, F, G, and H. For currents less than 10^{-8} ampere, the time rate of deflexion method was used, a one-microfarad subdivided condenser M being connected in parallel with the insulated quadrants. For larger currents the electrometer was shunted with a resistance of a megohm N, or any fraction thereof, and the steady deflexions observed.

Experiments showing that the Ionization is partly an Ionization of the Vapour.

Current-E.M.F. curves were obtained for both the positive and negative ionization from samples of cadmium iodide under different conditions of pressure and temperature. Table I. contains a representative set of data given under a pressure of 9 cm. and at a temperature of 450–5° C. Approximate saturation of currents in both tubes was obtained at a potential of ± 160 to ± 200 volts. The currents remained fairly constant under potentials ranging from 160

to 320 volts when ionization by collision occurred. The above remarks are applicable to positive and negative current-E. M. F. relations obtained at pressures of 9, 7, 3, 1, and 0·4 cm. In general it was impossible to obtain, during the first ten or fifteen minutes' heating, current readings which were of any value in determining the saturating potential. The very rapid initial rise or decay of the ionization, as exhibited in the curves in fig. 3, explains the difficulty. It was expedient, therefore, to determine the relations between current and potential in the regions of steady or slow decay with time effects.

TABLE I.

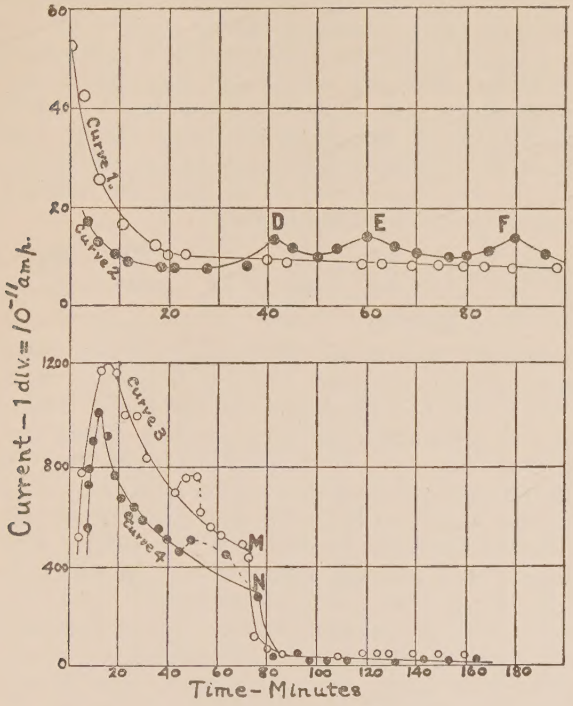
P=9 cm. Hg. T=450–5° C. 1 div.=1×10^{-10} amp.

Potential. (Volts.)	Current. (Tube A.)	(Tube B.)
+40	25·8	4·6
+80	46·9	11·7
+120	64·0	18·3
+160	80·0	22·5
+200	82·5	22·1
+240	85·0	26·8
−40	22·0	2·0
−80	41·5	2·9
−120	60·3	4·4
−160	70·8	5·4
−200	70·0	5·3
−240	73·2	6·7

The positive ionization was examined under a constant pressure of 1·3 cm. and at temperatures which ranged from 345° C. to 465° C. 300 mgms. of cadmium iodide were used in each case. Two sets of results are given in fig. 3; curves 1 and 2 show the current-time relations at a temperature of 385° C., curves 3 and 4 at 465° C., under the saturating potential of 200 volts. Curves 1 and 3 pertain to the ionization effects in the salted tube A. Curves 2 and 4, obtained with the unsalted tube B, show that *there can be an ionization in B when uncharged matter only enters it.* In fact the ionization in B may equal or exceed that of the salted tube. The current-time relations at 415° C. showed that the currents in B, initially equal to those in A, were after two hours' time twice or thrice as large. The ionization produced in both tubes when the temperature was below the

melting-point of CdI_2 (402° C. at atmospheric pressure) showed decay with time from initial maximum values. In contrast, curves 3 and 4, obtained at a temperature of 465° C., show a rise of current to a maximum value after

Fig. 3.



15–20 minutes' heating followed by values falling off asymptotically with the time. Also, the current-time relations, determined at a temperature of 415° C. and a pressure of 1·3 cm., showed a rapid rise in five minutes' heating to a maximum value of the current which was maintained for about twenty minutes and then decayed with time to a steady value after an hour's heating. These results at temperatures above 400° C. are not in accord with Schmidt's conclusion that the cadmium salts differ from other salts used in not exhibiting an initial rise, and that the products of decomposition, the active and inactive, have rates of decay, λ_1 and λ_2, which are nearly equal to each other. The results may be made to fit this explanation if λ_1 and λ_2 have about

equal values at the lower temperatures, but vary with the temperatures at different rates.

The maximum positive currents in the salted tube increased in the ratio of 20 : 1 in passing from a temperature of 350° C. to 415° C. at a pressure of 1·3 cm., the same quantity of salt being used in the two cases.

The ionization in tube B exhibited several maxima during the period of slow decay or steady valued currents in tube A. Points D, E, and F in curve 2 of figure 3 indicate such maxima. Also, at 415° C. it was found that the currents in A decayed asymptotically with the time from a value of 105×10^{-10} ampere at the thirty-minute point, to a steady value of 22×10^{-10} ampere after an hour's further heating. In the same interval of time the maxima and minima given below occurred in B :—

Time (min.)	50	60	73	80	92	120
Current	88	40	71	44	63	36

1 div. $= 10^{-10}$ ampere.

These secondary maxima appeared under different conditions of pressure and temperature. It is not likely that they were due to salt which had condensed on the cooler portions of the tube and fallen back, for these maxima did not occur in tube A which carried the salt and, moreover, they did not occur in the emission from the original salt, but were found in the ionization effects from the first distillate as tested by the air-cooled electrode method (see page 386). Professor Richardson * has recently reported work in which he was unable to obtain with cadmium iodide the specific charge characteristic of the cadmium atom. Values were obtained, however, showing the presence of sodium, potassium, and zinc. Complex chemical changes may, then, have taken place, causing these maxima and minima in the positive ionization, or else several substances present as impurities and having different decay constants may have been the sources.

A rapid fall in current values is shown in curves 3 and 4, figure 5, at the points M and N, followed immediately by a practically steady current condition of $5\text{–}10 \times 10^{-11}$ ampere covering a period of over an hour. These end effects indicate the disappearance of the salt and the rapid ionization of the salt vapour present in the tubes. The steady current stage may be attributed to the ionization from the platinum alone, or to the ionization from the products formed at the electrodes due to the interaction of the vapour and the platinum.

* Physical Review, xxxiv. p. 386 (1912).

When the temperatures were below 400° C., the melting-point of cadmium iodide, the greater portion of the salt inserted in A remained after the experiments had been made.

The effect of changing potential from positive to negative values, and *vice versa*, on the ionization in tubes A and B, was investigated at a temperature of 345–350° C. and a pressure of 1·3 cm. The positive current-time relations during the first twenty minutes of heating were identical with those represented in curves 1 and 2, figure 3. The steady current state, reached after 30–40 minutes' heating, furnished an excellent opportunity of studying the effects produced by a reversal of the electric field.

TABLE II.

1 div. $= 1 \times 10^{-11}$ ampere.

Tube			Tube B.		
Time. (Min.)	Volts.	Current.	Time. (Min.)	Volts.	Current.
25	+120	46·0	26	+120	9·6
27		43·2	28		9·6
31	−120	6·8	29	−120	46·0
33	+120	55·3	32		31·0
35		39·2	36	+120	8·9
37		34·3	39		7·3
42	−120	7·2	41	−120	33·0
44		3·4	43		12·3
46		2·6	45		7·6
48	+120	41·5	49	+120	9·5
52		25·0	53		6·2
55		18·2	57		5·2
59		15·3	60		4·7

An inspection of the results given in Table II. shows that a reversal of potential in tube A from positive to negative voltages gave negative current readings of about one-fifth to one-tenth the positive values immediately preceding. When the potential was again reversed, the positive readings were temporarily increased, but fell off asymptotically with the time and ultimately assumed values fitting upon a curve indicating the general decay with time of the positive ionization. The corresponding treatment of B showed the exact counterpart to the phenomena in A; since, for example, the reversal from a positive to a negative potential gave a current about five times as great as the previous positive

potential reading. Schmidt * investigated in detail the effects produced by a reversal of the electric field, using cadmium iodide at temperatures of 260° C. and 332° C. and a pressure of 3·7 mm. The results recorded in Table II. agree in general with those of Schmidt in the case of the effects observed in tube B. The results, however, in the salted tube A (which should be compared with Schmidt's results) are quite different.

The ionization produced by cadmium iodide under positive and negative potentials was further investigated by making use of a modification of the apparatus shown in fig. 1. The glass portions were similar in form to those previously described; the tubes were 15 cm. in length and 1 cm. in diameter. The arrangement of electrodes in tube B was the same as shown in figure 1. The inner electrode, however, of the tube carrying the salt consisted of a closed platinum cylinder fitted in symmetrically with respect to the outer platinum gauze. The distance between these two electrodes was 2 mm. It was thus possible to obtain saturation with greater surety, allowing the passage of uncharged matter only into B. The experiments with this apparatus were made at a temperature of 353–360° C. and at a pressure of 1 cm. Saturation was obtained in A for both positive and negative potential currents with 80–120 volts. Table III. contains data for representative current-E.M.F. curves.

Table III.

	Tube A.		Tube B.	
V	+	−	+	−
10	3·6	3·4	...	...
20	5·0	4·8	...	...
40	6·3	5·6	16·0	2·0
80	9·8	5·8	26·3	3·4
120	10·2	6·2	29·0	5·1
160	10·8	7·0	30·1	5·3
200	13·7	8·3	32·0	7·0

The current-time effects were examined in both tubes under the saturating potential of ±120 volts. The pressure was 1 cm. and the temperature 358–363° C. The ionization in the salted tube, under either a positive or negative potential, fell off from an initial maximum and reached the steady state after forty minutes' heating. This constancy

* *Loc. cit.*

and practical equality of positive and negative potential currents continued for two hours or more. Plenty of salt remained in A at the end of the experiment. The positive and negative current-time relations for A were identical in form with those given in curve 1, fig. 3. The values given for tube A in Table IV. are in excellent agreement with Schmidt's results. The ionization effects in the unsalted tube, however, showed marked contrasts with those obtained in the salted tube. The magnitude of both negative and positive potential currents in B in comparison with those in A (see Table IV.) is a most noticeable feature. Both currents in A had about the same value at corresponding times; in the unsalted tube the ratio of the initial negative maximum to the initial positive maximum was 7 : 1. These experiments fully confirm the statement that the ionization is partly an ionization of the vapour.

TABLE IV.

P = 1 cm. T = 358–363° C. 1 division = 10^{-10} ampere.

Time. (Min.)	Tube A.		Time. (Min.)	Tube B.	
	+	−		+	−
5	65		6	2347	
7		101	10		17745
11	13·3		12	1547	
13		30·3	14		16198
16	2·8		17	1183	
19		5·7	20		12103
22	1·26		23	819	
25		1·83	26		9100
28	0·61		29	637	
32		0·83	31		7462
37	0·43		35	455	
43		0·47	38		5187
53	0·38		48	192	
57		0·39	50		2366
			60	57	
			62		910
			67	27	
71	0·31		69		544
77		0·37	86	3·1	
			90		83
			98	2·3	
100	0·35		102		48
104		0·35	121	0·78	
			123		7·4
155	0·42		166	0·7	
157		0·41	169		1·4

Several attempts were made to carry out similar experiments with this form of apparatus at temperatures above the melting-point of cadmium iodide. Enormous irregularities

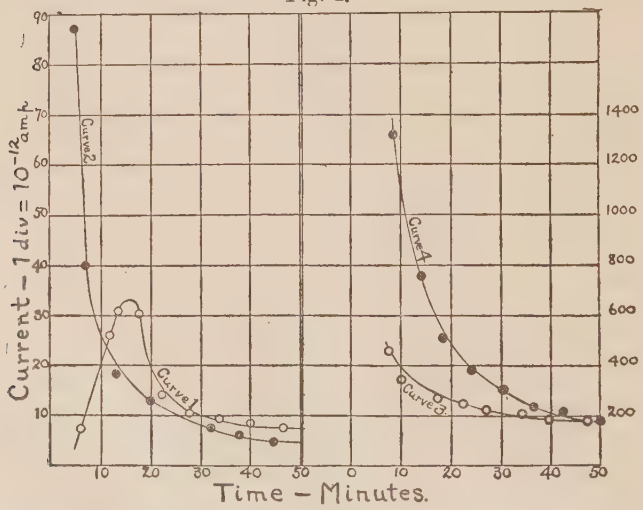
superimposed upon a rapid growth of current with time appeared soon after the heating had been commenced. Observation showed that the vaporized salt condensed on the cooler glass portions of the electrodes and finally bridged across, forming an increasingly better conductor as time went on.

Ionization Effects with Iodine and a Comparison with those given by Cadmium Iodide.

Shortly after the experiments just described (Table IV.) had been commenced, a heavy cloud of what seemed to be iodine vapour appeared in the unsalted tube B. There was little indication of its presence in other portions of the apparatus. This vapour condensed upon the cooler parts of the tube and electrodes and partially disappeared with time. The tube had a strong odour of iodine when opened. Similar phenomena were observed in other experiments.

These observations suggested that the liberation and ionization of the iodine constituent might play an important role in the current-time relations, especially in the effects observed in the unsalted tube. A considerable quantity of iodine was, therefore, inserted in A, and the conditions of the previous experiment, using cadmium iodide, as to temperature, pressure, and potential were duplicated. The current-time relations in the tube containing the iodine are

Fig. 4.



given in fig. 4, (o) indicating positive readings and (●) negative values. Curves 3 and 4 of this figure show the corresponding relations in tube B. These curves show that

the maximum currents obtained in both tubes under negative potentials exceeded the maximum positive currents in the ratio of 3 to 1. This is in agreement with results published by A. Campetti *, in which he showed that the electric dispersion in iodine with platinum electrodes and for temperatures up to 500° C. was greater for negative than for positive potentials.

The positive ionization with iodine in A rose to a maximum value in twenty minutes and then decayed with time. There is no similarity between the positive time-current relations in A, using iodine and cadmium iodide under similar conditions of pressure and temperature. The negative current curves are, however, comparable in form. The positive and negative current relations in tube B are similar in the two cases. The following ratios were found in the case of iodine (fig. 4) and cadmium iodide (Table IV.).

	Ratio.	I.	CdI_2.
(1)	$\frac{\text{Max. Negative in B}}{\text{Max. Negative in A}} =$	13	17
(2)	$\frac{\text{Max. Negative in B}}{\text{Max. Positive in B}} =$	3	6
(3)	$\frac{\text{Max. Positive in B}}{\text{Max. Positive in A}} =$	20	25

Considering the experimental difficulties involved, especially in getting the initial, and hence the maximum, current readings, it is fairly definitely proven that there is a *true negative ionization from cadmium iodide due to the iodine constituent.*

Emission of Ions from the Salt.—The Existence of Negative Ions.

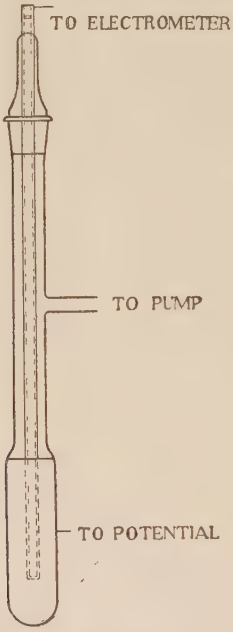
The existence of a current when the salt-covered plate, usually of platinum, is negatively charged, has been taken to indicate the emission of negative ions from the salt or volume ionization of the vapours given off from the salt. However, it might equally well arise from the vapour or the sublimed salt at the opposite electrode giving an emission of positive ions which would then saturate to the negatively charged electrode. For this reason the results with a hot detecting electrode, such as was used in the foregoing experiments and also by Schmidt in his work, may be equivocal. Furthermore,

* *Sci. Torino,* Atti, 40, 1, pp. 55–64 (1904–5).

chemical reaction* between the vapours and the heated electrodes may vitiate the true ionization effects.

In order, then, to obtain decisive tests as to the presence of a true negative ionization and to eliminate effects due to chemical action, the containing vessel was provided with an *inner air-cooled metallic electrode* and an *outer hot non-metallic electrode*. The apparatus used is shown in fig. 5.

Fig. 5.



It consisted of a glass tube 40 cm. long by 4·5 cm. diameter. The inner electrode was a quarter-inch brass tube sealed into the glass stopper with sealing-wax, and so adjusted that its lower end, closed air-tight with a brass plug, came about 1·5 cm. from the salt in the bottom of the main tube. It was kept cool by passing dry air under pressure through a glass tube slipped into the metallic tube. The temperature of this electrode rarely exceeded 50–75° C. after

* There was evidence of chemical action in the blackish appearance of the platinum electrodes. Hot aqua regia dissolved these films, but hot or cold acids or cold aqua regia had little effect. Ammonia readily removed them. Chemical tests, made after several experiments, showed traces of zinc, cadmium and a subiodide of platinum. The lower ends of the electrodes, which rested above the heated salt, became permanently black in colour and brittle after considerable usage.

the whole system had been heated for over an hour at 460° C. The glass vessel, the lower 15–20 cm. of which were inserted in the furnace, served as the outer heated non-metallic electrode. Auxiliary experiments showed that the glass was a good conductor of electricity in the vicinity of 300° C., the currents varying linearly with the applied voltages. Aluminium foil wrapped tightly about the outside of the tube and baked to the glass furnished a convenient method of connecting with the source of potential.

The modus operandi, connexions of the tube with the remainder of the testing system, &c., were essentially the same as those described in connexion with fig. 2. The empty tube, properly cleaned, when heated to 500° C. at low pressure gave currents of the order of 1×10^{-12} to 1×10^{-11} ampere.

Table V. contains a set of data for positive and negative current-E.M.F. relations obtained at 460° C. and 1 cm. pressure. These values were obtained in the steady current regions reached after an hour's heating under potential.

TABLE V.

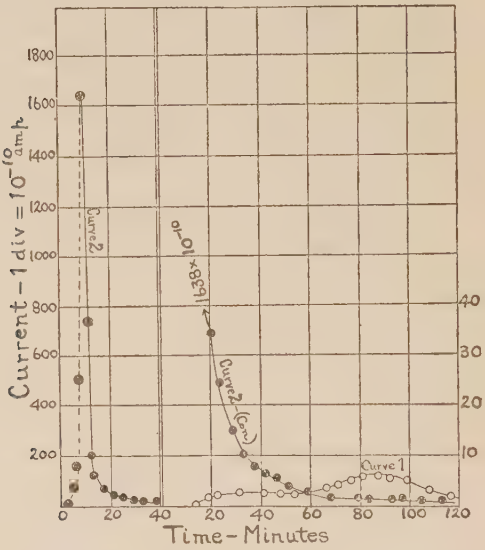
1 div. $= 10^{-11}$ ampere.

Potential.	+Currents.	−Currents.
0	0·1	0·05
10	2·1	
20	3·3	0·13
40	6·0	0·22
80	9·2	0·32
120	10·4	0·43
160	10·4	0·45
200	10·8	0·46

Two grams of cadmium iodide were heated at a temperature of 465–475° C. and at a pressure of 1·8–2 cm. under potentials of $\pm$ 200 volts. The current-time relations obtained are exhibited in fig. 6. Curve 1 (○) shows the positive and curve 2 (●) the negative current readings. The most noticeable feature is the quantitative relation existing between the maximum values of the negative and positive ionizations, for the former is over three hundred times as great as the latter. The negative current decayed from a value of 1638×10^{-10} ampere to 118×10^{-10} ampere during the first ten minutes. This was followed by the slow decay with time period for the succeeding forty minutes, after which

the current remained practically constant at a value of $2{\cdot}1 \times 10^{-10}$ ampere for over an hour. The dotted portion of curve 2, fig. 6, shows a rise of current to a maximum

Fig. 6.



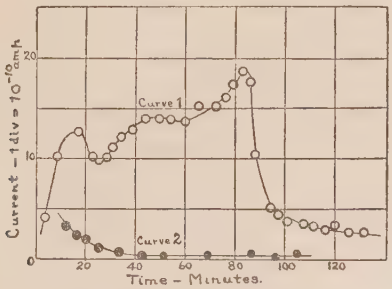
value after ten minutes' heating. This was not as definitely indicated in some similar experiments. It is difficult to say whether or not such a relation exists, since it is quite likely that there is a considerable temperature lag in the glass. To overcome this difficulty the furnace was heated about fifty degrees higher than the temperature required, the tube was then inserted and the currents in the heating apparatus regulated to values which experience had shown would give the desired constant temperature. The positive ionization increased slowly with time from a value of 1×10^{-10} ampere to a maximum value of $5{\cdot}8 \times 10^{-10}$ ampere after 80–100 minutes, followed by a slow decay period. It is of interest to note the dissimilarity in the positive current-time relations shown in curve 1, fig. 6, and curve 3, fig. 3. The temperature and pressure conditions were nearly identical in the two cases; the testing vessels were entirely different. The negative ionization effects are, however, in good accord with those recorded in Table IV., tube B. Other experiments similar to those described above were made at the same temperature and with the same quantity of salt, but at a pressure of 5–8 mm. The negative current fell initially

from a maximum value of 800×10^{-10} ampere to 8×10^{-10} ampere in seven minutes; the positive current increased with time from a value of $1{\cdot}7 \times 10^{-10}$ ampere to $12{\cdot}2 \times 10^{-10}$ ampere after 45–60 minutes' heating. These experiments, in toto, show conclusively that *there is an emission of ions from the salt, and that there are negative as well as positive ions.*

The Ionization Effects from the Distillates.

Various distillates collected on the cool inner electrode were re-run at the same temperature and pressure as the original sample of salt. The first distillate from the original salt at a pressure of 2 cm. and a temperature of 465° C., showed a negative ionization falling off with time from a maximum value of 260×10^{-10} ampere in a manner analogous to curve 2, fig. 6. The positive current-time relations, however, differed considerably from those shown in curve 1, fig. 6. Three distinct current maxima were exhibited after 20, 40–45, and 80–90 minutes' heating; this third maximum, the greatest of the three, had a value of 22×10^{-10} ampere in comparison with $5{\cdot}8 \times 10^{-10}$ ampere shown by the original salt. The positive ionization curve for the second distillate is given in curve 1, fig. 7, and is practically the duplicate of

Fig. 7.



that given by the first distillate. The negative current (curve 2, fig. 7) had an initial maximum value of $3{\cdot}2 \times 10^{-10}$ ampere. These curves show that the ratio

$$\frac{\text{Maximum Negative Emission, Original Salt}}{\text{Maximum Negative Emission, Second Distillate}} = 500 \text{ (roughly),}$$

and that

$$\frac{\text{Maximum Positive Emission, Original Salt}}{\text{Maximum Positive Emission, Second Distillate}} = 0{\cdot}33.$$

Two grams of cadmium iodide were originally used, and 750 mgms. of the second distillate were recovered and used as described above. Ten distillates from this original sample of salt were re-tested; alternations of greater negative or positive emission occurred. The power which the distillates had of producing negative ionization was in no wise comparable to that of the original salt; on the other hand, the positive ionization was considerably greater in certain of the distillates.

The results showing the maximum values of the positive and negative currents at a temperature of 465° C. and a pressure of 0·8 cm. are given in Table VI.

TABLE VI.

$P = 0{\cdot}8$ cm. Hg. $T = 465°$ C. 1 div. $= 1 \times 10^{-10}$ ampere.

Substance.	Maximum Negative.	Maximum Positive.
Original CdI_2	800·0	10·5
1st distillate	0·9	30·0
2nd distillate	92·0	3·2
3rd distillate	1·2	16·6
4th distillate	54·2	5·1

These figures show that the ratio of

$$\frac{\text{Maximum Negative Emission, Original Salt}}{\text{Maximum Negative Emission, First Distillate}} = 900 \text{ (roughly)},$$

and that the

$$\frac{\text{Maximum Positive Emission, Original Salt}}{\text{Maximum Positive Emission, First Distillate}} = 0{\cdot}34.$$

No explanation can, as yet, be offered why these distillates exhibit such alternations in their powers of negative and positive emission. No visible differences existed in the colour or general appearance of the distillates and the original salt. It seemed possible that the presence or absence of moisture might account in part for the marked dissimilarities in the ionization from the distillates. To this end the sixth and seventh distillates in the experiments at 2 cm. pressure were, in turn, treated with about a gram of water, and the negative and positive current-time relations determined.

No effects were observed in contradiction to the facts already set forth. *Nor can the large negative emission from the original salt be attributed to moisture.* A thick paste of fresh salt of about 3 grams weight was made and the ionization effects determined at a pressure of 1·8 cm. and a temperature of 480–90° C. The negative current fell off asymptotically with the time from a maximum of 200×10^{-10} ampere, a value about one-eighth of that shown in curve 2, fig. 6. The positive ionization, however, from the moistened salt was increased tenfold. When the distillate was removed from the inner electrode it was found coated on the inside with a thin blackish coloured film, a phenomenon which was not observed in other experiments.

Chemical Analyses of the Distillates.

Chemical analyses were made as to the percentage of iodine in (1) a sample of the cadmium iodide (Einer and Amend) used, (2) of the fifth distillate obtained at 1 cm., and (3) of the tenth distillate at 2 cm. pressure. The following percentages of iodine were found: (1) 72·14, (2) 70·27, and (3) 65·85. Hence *continued distillation diminishes the percentage of iodine.* This fact lends further support to the view that *the negative ionization consists in large part of the iodine constituent.*

Conclusions.

The following points have been fairly definitely established:—

(1) There can be an ionization in the secondary chamber B when only uncharged matter enters B, since there is a saturating potential in A. Thus the ionization is partially an *ionization of the vapour.* This may arise from the action of the vapour on the electrodes or it may be a volume ionization, or both.

(2) In addition there is an *emission of ions from the salt*, as shown by the experiments with the air-cooled electrode apparatus. Furthermore, the presence of *negative ions* is definitely proven. There is a large initial negative emission and practically no positive on heating a sample of the original salt. As the heating continues the positive ionization increases to a maximum and then falls away; the negative continually diminishes.

(3) The ionization in the unsalted tube B may equal or

exceed that in A, and the currents change in a different way when the direction of the applied field is reversed. The fact that the ionization in the tube B can be greater than that in the salted tube A seems to indicate that a great deal of the ionization arises from a substance which takes some time to form. Thus there may be more of this substance in the vapour by the time it has diffused into the tube B than there was when it was first given off by the salt.

(4) At temperatures below 402° C., the melting-point of CdI_2, the positive ionization effects in both tubes decay asymptotically with the time from an initial maximum value ; when the temperature is above this point the positive ionization increases with time to a maximum followed by decay with time.

(5) Iodine alone gives quite large currents. A comparative study of cadmium iodide and iodine shows that some, at least, of the negative ionization effects are probably due to the subsequent ionization of the iodine vapour which is liberated by chemical dissociation in visible quantities.

(6) The distilled salt is less active than the undistilled. The successive distillates exhibit alternations in their power of negative and positive emission. Those distillates which show a comparatively large negative emission exhibit a small positive ionization and *vice versa*. In the case of the distillates in which the negative emission is small the positive emission exceeds that of the original salt.

(7) Continued distillation diminishes the percentage of iodine in the salt, but does not produce much, if any, change in its appearance.

Several points suggested by these results are being tested by further experiments.

In closing this paper the writer expresses his thanks to Professor O. W. Richardson, who suggested this line of research, and to whom he is indebted for many suggestions during its progress. He also wishes to thank Mr. C. Bol for the construction of the various pieces of glass apparatus used.

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